



Development of a rapid ageing technique for modern methane combustion catalysts in the laboratory: Why does SO₂ concentration play an essential role?

Paavo Auvinen^a, Niko M. Kinnunen^{a,*}, Janne T. Hirvi^a, Teuvo Maunula^b, Kauko Kallinen^b, Matthew Keenan^c, Rik Baert^d, Erik van den Tillaart^d, Mika Suvanto^a

^a University of Eastern Finland, Department of Chemistry, P.O. Box 111, FI-80101, Joensuu, Finland

^b Dinex Ecocat Oy, Global Catalyst Competence Centre, P.O. Box 20, FI-41331, Vihtavuori, Finland

^c Ricardo UK Ltd, Shoreham Technical Centre, Shoreham-by-Sea, West Sussex, BN43 5FG, United Kingdom

^d TNO, P.O. Box 756, 5700 AT Helmond, the Netherlands

ARTICLE INFO

Keywords:

Sulphur
Deactivation
Poisoning
Palladium sulphate
Natural gas

ABSTRACT

In pursuance to decrease emissions of transportation sector, the durability and longevity of modern catalysts has become a topical issue. Understanding the deactivation of catalysts is especially urgent. Our aim in this study was to clarify the roles of reaction temperature and SO₂ concentration in methane combustion catalyst poisoning. Information about this process can help the research community perform more realistic laboratory simulations and provide new insights for catalyst development. With the collected experimental data, the likelihood that poisoning would be influenced by different sulphur species and mechanisms was evaluated. Our results suggested that both reaction temperature and SO₂ concentration influenced the stability of the resulting sulphates. Low SO₂ concentrations lead to formation of stabler sulphates and lower total amount of sulphur in the catalyst. In turn, high SO₂ concentrations formed less stable sulphates but accumulated more sulphur. Lesser stability was attributed to formation of Al₂(SO₄)₃ through spillover.

1. Introduction

The urgent need to reduce global carbon emissions became particularly apparent following the autumn 2018 release of the special report on global warming by the Intergovernmental Panel on Climate Change (IPCC) [1]. According to this report, it is highly probable that the global mean temperature will increase by 1.5 °C above pre-industrial levels sometime between 2030 and 2052. Consequently, the hazards related to increasing temperature are bound to become more severe. As the global demand to reduce emissions of greenhouse gases (GHGs) and other pollutants grows, interest in alternative fuels in the transportation sector has steadily increased. However, this transition is not straightforward, and many engine applications require additional research before their commercial use will be feasible. Natural gas lean-burn engines are of growing interest, especially in the European Union (EU). This interest originates from the European Parliament's objective to reduce GHG emissions by 60% from the 1990 level by the end of 2050 [2]. In addition to increasing alternative fuel consumption, improved and more durable emission after treatment systems are vital as well.

Emissions research has revealed that lean-operating natural gas engines produce low amounts of CO₂ compared to diesel engines [3–5]. Compared to diesel fuel, the low carbon-to-hydrogen ratio of methane directly reduces the amount of CO₂ released into the atmosphere during combustion [6]. Other benefits of natural gas include ease of transport and storage. As can be expected, there are also disadvantages related to natural gas utilization. The most problematic of these is methane slip from the engine, which is the discharge of methane into the exhaust gas stream. The global warming potential (GWP) of methane is 28-fold higher than that of CO₂ [7]. This is a major concern, because traditional three-way catalysts and diesel oxidation catalysts are not optimal for methane combustion.

Durability requirements for heavy-duty vehicles in Europe were established by EU regulation 595/2009 [8]. To satisfy these requirements, increasing the durability of catalysts is necessary. Catalyst deactivation can be caused by thermal effects, such as sintering and phase transformation, or it can occur chemically through poisoning [9–11]. Indeed, catalyst deactivation is one of the greatest challenges in environmental catalysis research. Accordingly, several groups have

* Corresponding author.

E-mail address: niko.kinnunen@uef.fi (N.M. Kinnunen).

<https://doi.org/10.1016/j.apcatb.2019.117976>

Received 1 April 2019; Received in revised form 11 July 2019; Accepted 17 July 2019

Available online 24 July 2019

0926-3373/ © 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

studied the effects of the gas atmosphere on catalysts by performing catalyst ageing and regeneration simulations in the laboratory [12–15]. These operations are often referred to in the literature as rapid ageing techniques. However, our understanding of catalyst ageing and poisoning processes is still deficient. Rapid ageing is a useful test method, as actual on-road experiments are both time-consuming and costly. Laboratory testing in turn can yield results more quickly in a controlled environment. However, there is significant variation among both ageing methods and regeneration techniques. Markedly different exhaust gas compositions and ageing temperatures are applied across the field. Consequently, much uncertainty still exists with regard to catalyst ageing conditions.

It is a widely held view that bimetallic Pd-Pt catalysts have the highest activity for methane combustion [16]. The Pd-PdO interface is thought to be the active phase at low temperatures and under lean operating conditions [4,11,17]. Thus, modern methane oxidation catalysts (MOC) typically contain Pd. It has been proposed that the presence of Pt affects bonding between Pd and O by weakening the bond to enhance catalytic activity [16]. Additionally, a small amount of Pt has been found to improve resistance to sintering [18]. Based on previous research [16,19], it is clear that Pd is vulnerable to sulphur poisoning, whereas monometallic Pt exhibits resistance to it. The existence of platinum sulphates has not yet been proved experimentally, although a theoretical study of the subject has been published [20]. Nevertheless, experiments have shown that addition of Pt to a catalyst can promote the resistance of Pd to sulphur poisoning [18].

In addition to methane, natural gas contains higher alkanes and sulphur, namely H₂S. Sulphur possesses a reactive electron pair and is a known transition-metal catalyst poison [9,10,21–23]. Even trace amounts of sulphur in exhaust gas are readily oxidized to SO₂, leading to the formation of PdSO_x and ultimately bulk PdSO₄ [10,24,25]. According to many in the field, catalyst deactivation is associated with sulphate formation, a phenomenon generally referred to as catalyst poisoning. Recent research suggests the culprit is actually a combined effect of water and sulphur [22]. This interpretation contrasts with the traditional view, which is that lone sulphates cause poisoning. The accession of the light-off temperature (T₅₀) due to water is well documented [4,10,22].

Gremminger et al. performed laboratory-scale ageing experiments, and they reported that low SO₂ concentrations (≤ 5 ppm) affected the poisoning rate [26]. However, a search of the literature reveals that the SO₂ concentrations used in MOC ageing experiments over the last two decades range from 2.5 to 500 ppm [10,18,26–28]. In the present work, we studied the rapid ageing process in CH₄ combustion simulations to gain a better understanding of the effects of SO₂ concentration and reaction temperature. We aimed to address three research questions. First, how does SO₂ concentration affect CH₄ conversion during the poisoning process? Second, is there a relationship between SO₂ concentration and sulphur accumulation in the catalyst? Finally, do temperature and SO₂ concentration affect sulphate stability?

2. Materials and methods

2.1. Catalyst

Dinex Finland Oy provided the catalysts for the laboratory simulations. The catalyst contained Pd and Pt in a weight ratio of 4:1, with a total noble metal loading of 7.06 g/L. High-surface area γ -alumina (γ -Al₂O₃) served as the support material. The wash coat was deposited over a corrosion-resistant metallic foil by the open-foil coating method.

2.2. Characterization and ageing measurements

The exact gas concentrations used for the ageing experiments along with other reaction parameters are summarized in Table 1. Catalyst ageing was examined at 400 °C, 430 °C, 450 °C and 500 °C at SO₂

Table 1

Compositions of the ageing gas mixtures used for catalyst measurements.

Gas	10 ppm SO ₂	50 ppm SO ₂	100 ppm SO ₂
CH ₄	2000 ppm	2000 ppm	2000 ppm
CO	2000 ppm	2000 ppm	2000 ppm
NO	500 ppm	500 ppm	500 ppm
CO ₂	6%	6%	6%
O ₂	10%	10%	10%
H ₂ O	10%	10%	10%
N ₂	balance	balance	balance
SO ₂	10 ppm	50 ppm	100 ppm
Treatment duration	10 h	2 h	1 h
Total amount of SO ₂	294 μ mol	294 μ mol	294 μ mol
GHSV	50,000/h	50,000/h	50,000/h

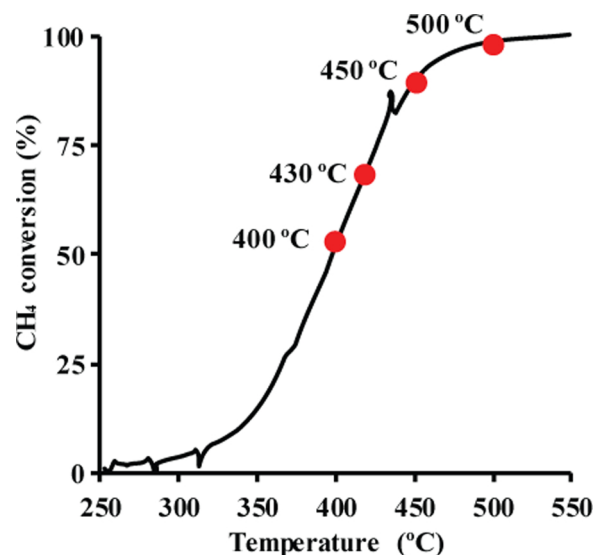


Fig. 1. Light-off curve of a modern methane combustion catalyst. The red circles indicate the temperatures used for the ageing measurements (For interpretation of the references to colour in this figure Legend, the reader is referred to the web version of this article).

concentrations of 10 ppm, 50 ppm and 100 ppm. A light-off curve obtained with a fresh MOC at the temperatures selected for our tests is shown in Fig. 1. The selected temperatures are typical in a lean-operating natural gas engine [29]. By varying the ageing time, the amount of sulphur exposed to the catalyst was held constant at 294 μ mol. The catalysts were shaped into cylinders 18 mm in height and 10 mm in diameter, which contained a noble metal loading of 0.01 g per cylinder. The cylinders were positioned inside a reactor tube. During the experiments, the reactor contained 65 μ mol PdO. The reactor tube was then placed in a furnace and connected to a gas stream. The gas atmosphere was established with GF Series mass-flow controllers (Brooks Instrument, Hatfield, PA), and the gas hourly space velocity (GHSV) was fixed at 50,000/h. The gas atmosphere was comprised of CH₄, CO, CO₂, NO, O₂ and H₂O, while N₂ served as the balancing gas. Prior to the ageing treatments, each catalyst was stabilized at 600 °C. Ageing measurements were performed under steady gas flow at a constant temperature. Gas concentrations were recorded with a FTIR multi-gas analyzer (Gasetm, Finland) downstream of the catalyst during each measurement. During the light-off phase, the oven was heated at a rate of 7 °C/min. To prevent possible sulfate decomposition and additional SO₂ chemisorption following each ageing measurement, the samples were cooled in a 10% O₂/N₂ atmosphere.

After each ageing treatment, the catalyst was scraped from the monolith. The sulphur content of each sample was measured with a vario Micro cube elemental analyzer (Elementar, Germany). The device was calibrated with sulfanilamide and sulfamethazine served as a

known reference that verified the calibration was successful. Measurements were performed with aged samples before and after the temperature-programmed oxidation (TPO) process.

Steady state engine testing was performed over a range of different speed and load points to characterise the MOC efficiency pre and post ageing. The steady state key points were determined to give an appropriate range of catalyst temperatures and space velocities in order to characterise the light-off for methane control. The catalyst temperature ranged from 250 to 580 °C and the space velocity ranged from approximately 20,000–80,000 1/h. The pre-catalyst methane emissions ranged from 350 to 3000 ppm.

The chemical state of each catalyst was then examined by TPO analysis in an 0.1% O₂/He gas atmosphere. The sample size for each TPO measurement was approximately 100 mg, and the collected data was standardized by weight. An Autosorb-iQ gas sorption analyzer (Quantachrome Instruments, Boynton Beach, FL) equipped with a thermal conductivity detector (TCD) and an integrated quadrupole mass spectrometer were used to analyze the desorbed gases. Low oxygen content yielded better apparent peak separation in the TCD contour plots. The heating rate in the TPO was 10 °C/min with ramping from room temperature to 1000 °C. Water was largely prevented from entering the TCD through the use of a cold trap.

3. Results and discussion

3.1. Poisoning process and methane conversion during ageing

Rapid-ageing techniques should be performed quickly yet still provide results that correlate well with those obtained with a real engine. There is a good general agreement between laboratory and real-engine experiments for CH₄ conversion with the fresh MOC and poisoned MOC as illustrated in Fig. 2. The test-bed experiment protocol is considered confidential information, but the results are accounted comparable. The tests are performed on the same catalyst and 50 ppm SO₂ was used in both the laboratory and real-engine experiments. For comparison, natural gas contains approximately 1 ppm S in the form of H₂S, which under lean conditions is oxidized to SO₂ [6]. The precise quantity of S in the natural gas depends on the region from which it is harvested. Some differences between test-bed and laboratory test results as well as the data scattering could result from space velocity variations in the engine

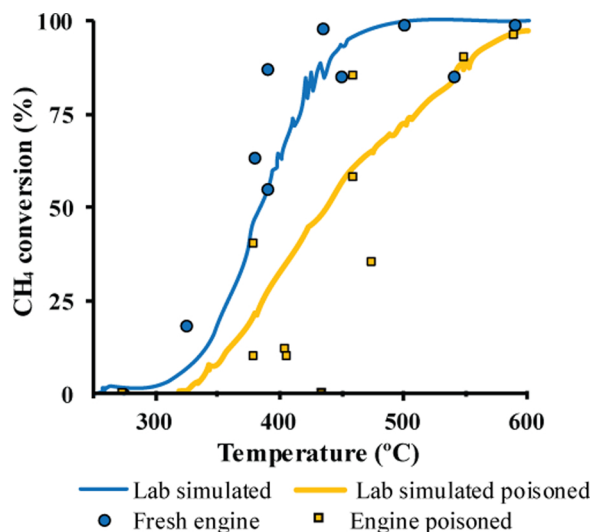


Fig. 2. Correspondence between CH₄ conversion results obtained from laboratory light-off experiments (solid lines) and an engine test stand (points) using fresh catalyst (blue) and a catalyst poisoned under 50 ppm SO₂ (yellow) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

tests, temperature transients during engine testing, and other factors such as S-containing compounds in oil [29]. To an extent, the suitable SO₂ concentration for conducting well-correlating rapid ageing simulations is a matter of speculation.

We studied the effect of SO₂ concentration over a broad range to gain information that reflected realistic rapid-ageing conditions. We thus performed a series of measurements with 10 ppm, 50 ppm and 100 ppm SO₂. Lean-burn NG and biogas engines operate in the temperature range of 400–500 °C most of the time. Hence, we performed the poisoning experiments at typical operating temperatures for these engines (400 °C, 430 °C, 450 °C and 500 °C).

Fig. 3 contains the acquired CH₄ conversion contour plots, which are grouped according to temperature. It should be noted that although we supplied the same amount of sulphur at each temperature, the poisoning durations at different SO₂ concentrations were not identical. Consequently, CH₄ conversion is presented as the percentage of poisoning progression. This way, at a given point on the x-axis, the amount of sulphur entering the catalyst is the same. The error of the FTIR device was 2%, but the error bars are not presented for the sake of clarity. Measurements performed near the light-off region (400 °C and 430 °C) showed large variations in CH₄ conversion due to high-temperature sensitivity (Fig. 1). This is especially visible in Fig. 3a, in which the conversion starting points at the three SO₂ concentrations differ. Overall, the conversion curves in Fig. 3a and b overlapped rather well with only small deviations. We speculated that less SO₂ desorbed at 400 °C and 430 °C, which in turn promoted the oxidation of SO₂ to SO₃ and ultimately to PdSO₄. Thus, most of the sulphur remained in the catalyst at these temperatures regardless of SO₂ concentration.

Measurements performed at higher temperatures indicated greater catalyst stability, so the CH₄ conversion starting points were similar. Additionally, the conversion curves diverged at an earlier stage of progression. It was noted that in Fig. 3c (450 °C) and Fig. 3d (500 °C), conversion at the end of the measurements was higher with 10 ppm SO₂ than with either 50 ppm or 100 ppm SO₂. Furthermore, the greatest extent of deactivation was observed at a SO₂ concentration of 50 ppm. Thus, catalyst deactivation was intriguingly non-linear with respect to SO₂ concentration. The rate of deactivation was evidently bound to SO₂ concentration. These observations led us wonder whether dissimilar SO₂ concentrations could lead to formation of different SO_x structures on the catalyst. In other words, could the SO₂ concentration possibly affect the poisoning mechanism via spillover? During spillover, SO₂ or SO₃ molecules migrate from the precious metals into the support material and form sulphates. Prior studies have noted spillover to be a plausible mechanism for reducing deactivation of Pd/Al₂O₃ catalysts [10,18,27] and it has also been studied on Pt/Al₂O₃ based Diesel oxidation catalysts [30–32]. To enable further predictions, the next step was to determine how much sulphur bound to the catalysts during the poisoning process.

3.2. Elemental analysis

Elemental analysis of the samples was performed after the ageing treatments. In Fig. 4a, the quantity of bound sulphur following treatment at each temperature is shown according to SO₂ concentration. The average standard deviation of the mean of the sulphur measurements was 0.01, while the largest individual error was 0.05. The error could thus be considered insignificant, which is why error bars are not shown in the figure. Catalysts poisoned with 10 ppm SO₂ gathered the least amount of sulphur. This was consistent with the results shown in Fig. 3c and d from samples in which conversion with 10 ppm SO₂ remained the highest. The sulphur content varied less with temperature in the samples poisoned with 50 ppm and 100 ppm SO₂, although samples treated with 50 ppm SO₂ at 400 °C and 450 °C contained slightly more sulphur. The same results are plotted in Fig. 4b with respect to reaction temperature. The highest amount of sulphur accumulated on catalysts that were poisoned at 400 °C. In general, the sulphur content decreased

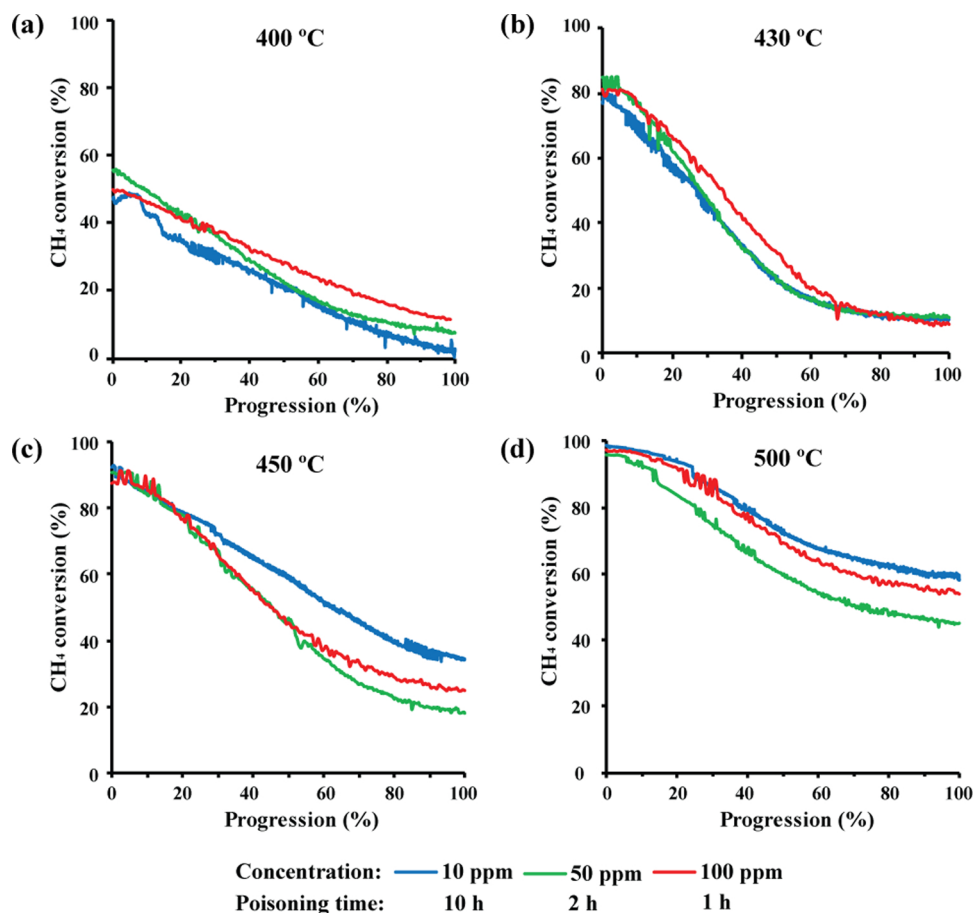


Fig. 3. CH₄ conversion curves at (a) 400 °C, (b) 430 °C, (c) 450 °C and (d) 500 °C. The SO₂ concentration is indicated by colour: 10 ppm (blue), 50 ppm (green) and 100 ppm (red). The base gas mixture contained 10% O₂, 6% CO₂, 2000 ppm CO, 500 ppm NO and 2000 ppm CH₄ (For interpretation of the references to colour in this figure Legend, the reader is referred to the web version of this article).

gradually with increasing temperature. Gremminger et al. previously observed more vigorous catalyst poisoning at 400 °C than at higher temperatures [26]. Our measurements were in accordance with these results.

To acquire additional insight into sulphur accumulation, we examined the relationship between the amount of bound sulphur in our catalysts and the amount of sulphur that was introduced to them via the gas stream. These results are summarized in Table 2. The percentage of sulphur in the gas stream that was retained by the catalysts varied from 13.0% to 25.7%. We also compared the amount of sulphur gathered by the catalysts with the quantity of sulphur in 65 µmol of PdSO₄, the theoretical maximum. The latter values spanned from 58.8% to over 116.1%, as can be seen in the table. Catalysts poisoned with 50 ppm and 100 ppm SO₂ at 400 °C and 430 °C contained especially large quantities of sulphur, even though conversions in the Fig. 3 are similar with a catalyst poisoned with 10 ppm SO₂. The 50 and 100 ppm samples actually exceeded 100% of the theoretical maximum, which was the upper limit of the amount of sulphur that could be bound to Pd. This could be attributed to formation of Al₂(SO₄)₃, which can form directly or as a spillover product. The 10 ppm samples gathered the smallest quantities of sulphur, and the amounts became even smaller with increasing temperature.

Overall, the results confirmed that both SO₂ concentration and reaction temperature influenced the amount of sulphur bound by the catalysts. Earlier, we speculated about the formation of different SO_x structures and reaction mechanisms in relation to SO₂ concentration. The results of the conversion measurements (Fig. 3) and elemental analysis (Fig. 4) validated this line of thought. We propose that higher SO₂ concentrations may promote spillover of SO_x as the competition for active sites becomes more severe. PdO/Pd ratio has been shown to decrease due to oxidation reactions already during light-off of the

catalyst [12]. Sulphur in spillover can coordinate with the support to form Al₂(SO₄)₃, which explains the larger quantities of sulphur in samples treated with 50 ppm and 100 ppm SO₂ (Fig. 4, Table 2). Honkanen et al. observed this experimentally when they detected Al₂(SO₄)₃ on a MOC that was poisoned with 100 ppm SO₂ [27] and it has also been detected on Pd-Pt/Al₂O₃ model catalysts as well as commercial Pt/Al₂O₃ Diesel oxidation catalysts [18,31,33]. In the present study, at elevated temperatures (450 °C and 500 °C) catalysts poisoned with 10 ppm SO₂ gathered less sulphur and retained higher conversion, as spillover effects were not as likely as with 50 ppm and 100 ppm SO₂. At lower temperatures (400 °C and 430 °C) 10 ppm SO₂ gathered similarly fewer amount of sulphur, however the conversion was equal to that of the samples poisoned with 50 ppm and 100 ppm. As already speculated in Section 3.1, this can be explained with the lower desorption rate of sulphur, which causes active sites to be saturated efficiently also with low SO₂ concentrations.

With regard to the reaction mechanism, reduction of the PdO to metallic Pd occurs more rapidly at high SO₂ concentrations due to oxidation to SO₃. This increases the number of metallic Pd sites. It can thus be speculated that SO₃ cannot readily form PdSO₄ in these conditions. Instead, spillover becomes a more optimal route for SO₃ to form sulphates, i.e. Al₂(SO₄)₃. In addition, oxidation of SO₂ to SO₃ might become more favourable on the support as well. At low SO₂ concentrations, however, there are more PdO sites available, on which these oxidation reactions can proceed. Intuitively, this would lead to the formation of larger and stabler sulphate structures, namely bulk PdSO₄. Moreover, it has been shown that Al₂(SO₄)₃ may hinder re-oxidation of Pd to PdO in catalyst regeneration [34]. Assuming the re-oxidation tendency is connected to oxygen exchange between the support and the noble metal, this would at least partially explain why the samples poisoned under 10 ppm SO₂ maintain higher conversion

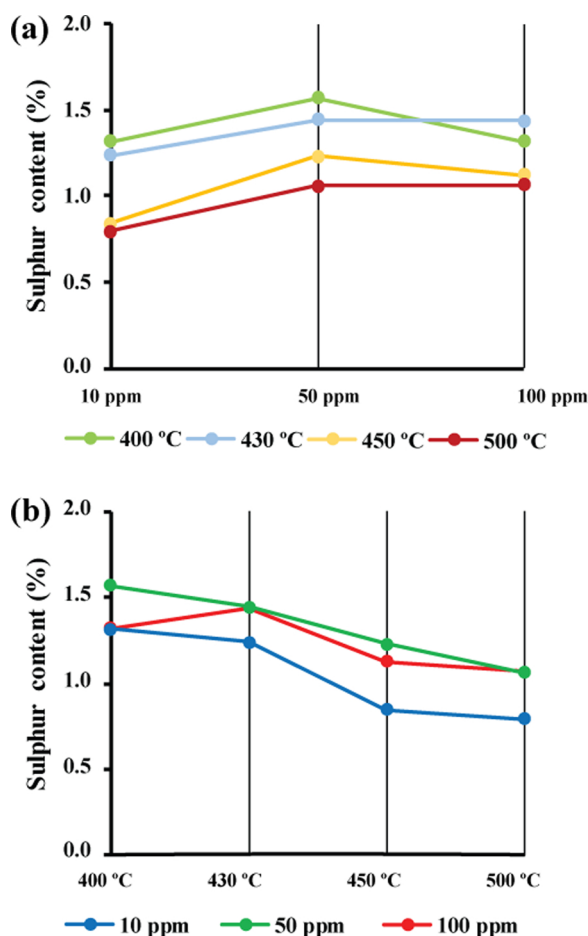


Fig. 4. Results of sulphur analysis for catalyst samples following ageing treatment as a function of (a) SO₂ concentration and (b) temperature.

Table 2

The amount of sulphur bound by the catalysts as a percentage of sulphur entering during the poisoning process and as a percentage of the theoretical maximum (PdSO₄) in a MOC.

	% Sulphur in the gas mixture retained by the catalyst			% Theoretical maximum (PdSO ₄)		
	10 ppm	50 ppm	100 ppm	10 ppm	50 ppm	100 ppm
400 °C	21.5%	25.7%	21.6%	97.2%	116.1%	97.5%
430 °C	20.3%	23.7%	23.6%	91.7%	106.8%	106.5%
450 °C	13.8%	20.2%	18.4%	62.5%	90.9%	83.2%
500 °C	13.0%	17.4%	17.5%	58.8%	78.4%	78.7%

during poisoning at high temperatures (Fig. 3). There has been previous research on support-noble metal interactions in oxygen exchange [35–37]. Motivated by these observations, we subjected every sample to TPO treatment to learn more about sulphate stability in our poisoned catalysts.

3.3. TPO treatment

The literature contains various temperatures at which the sulphur is desorbed from the catalyst during heating [18,22,33,38]. These variations result from different poisoning and desorption conditions during heating. A recent study on PdSO₄/Al₂O₃ model catalysts revealed the differences in SO₄ degradation under various conditions [38]. It was found that inert conditions destabilises PdSO₄ more in respect to oxidizing conditions (TPO). Moreover, Wilburn et al. showed that Pd rich

bimetallic catalysts form sulphates that can stand significantly higher temperatures than Pt rich catalysts [33]. Our results of the TPO measurements are shown in Fig. 5. The large increases in TCD signal intensity observed above 600 °C originated from decomposition of sulphate to O₂ and SO₂. This was evident in the concurrently obtained quadrupole mass spectrometry results. The results of O₂ and SO₂ quantitation by mass spectrometry mirrored the TCD curves. The observed sulphate decomposition can be attributed to PdSO₄ as previous research insinuates that Al₂(SO₄)₃ degradation requires above 950 °C temperature [39]. The stepwise degradation of SO₄ into O₂ and SO₂ is in line with TCD and quadrupole mass spectrometry results reported in a previous study [22]. According to elemental analysis virtually all sulphur has left the sample in post-TPO samples. Results from analysis of fresh MOC samples are shown in Fig. 5 for reference. In the plots for the fresh samples, the peak above 600 °C originated from PdO decomposition to metallic Pd and was thus associated with O₂ desorption. It was worth noting that the peak maxima of the fresh samples were observed at lower temperatures than those of the poisoned catalysts. This was in accordance with the mass spectrometry results, which suggested that O₂ began to desorb before SO₂ during sulphate decomposition.

The TCD contour plots of samples poisoned at 450 °C and 500 °C are shown in Fig. 5c and Fig. 5d, respectively. Again, the differences identified at different SO₂ concentrations were most visible in these samples, since the temperature was clearly above T₅₀. There was an obvious shift in the TCD peak maxima to higher temperatures with decreasing SO₂ concentration. This implied that catalysts poisoned with 10 ppm SO₂ contained stabler sulphates. In Fig. 5a and b, the separation is more modest. The most likely reason for this was proximity to the light-off region.

If the same measurements are grouped according to SO₂ concentration, it can be seen that stabler sulphates form at higher temperatures. This is illustrated in Fig. 6 and corresponds well with the findings of Gremminger et al. [26]. This trend is especially clear in Fig. 6a and b, which show the contour plots of the 10 ppm and 50 ppm samples, respectively. Results from the catalysts poisoned with 100 ppm in Fig. 6c do not reflect such large variation. A possible explanation for this may be the spillover of sulphates. As we suggested in Section 3.2, high SO₂ concentrations may promote spillover and lead to the formation of Al₂(SO₄)₃ instead of PdSO₄.

We also integrated the TCD curve areas from 500 °C forward. The area trend was consistent with the results of elemental analysis, and the curves of the 10 ppm samples had smaller areas than those of samples poisoned with higher SO₂ concentrations. It should be noted that the TCD curves included the desorption of O₂ in addition to SO₂, which affected the integration results.

The results from our investigation of sulphate stability shown in Figs. 5 and 6 support the elemental analysis results shown in Fig. 4. This, along with supporting literature suggest that the large peaks above 600 °C arise from degradation of stable structures that include sulphur, i.e. sulphates [22,33,38]. Sulphates that decompose below 950 °C are attributed to PdSO₄ rather than Al₂(SO₄)₃. Low SO₂ concentration (10 ppm) yielded PdSO₄ sulphates which decompose at higher temperatures in comparison with samples that are poisoned with high SO₂ concentrations (50 ppm and 100 ppm). According to recent research, the formation of Al₂(SO₄)₃ due to the spillover destabilizes PdSO₄ [34,39]. Hence, the less stable sulphates that are formed by using high SO₂ concentrations can be explained with the spillover and larger formation of Al₂(SO₄)₃. In other words, the SO₂ concentration affects the relation in which Al₂(SO₄)₃ and PdSO₄ are formed, which consequently can be seen as a shift in a TCD curve. Furthermore, spillover may also explain why the catalyst poisoned at 50 ppm SO₂ experienced stronger deactivation and have gathered generally more sulphur in respect to samples poisoned at 10 ppm or 100 ppm SO₂. With higher concentration the formation of Al₂(SO₄)₃ is more optimal route for SO₂ or SO₃ to react with oxygen, which leaves larger amount of precious metal sites unpoisoned, thus explaining the non-linearity of

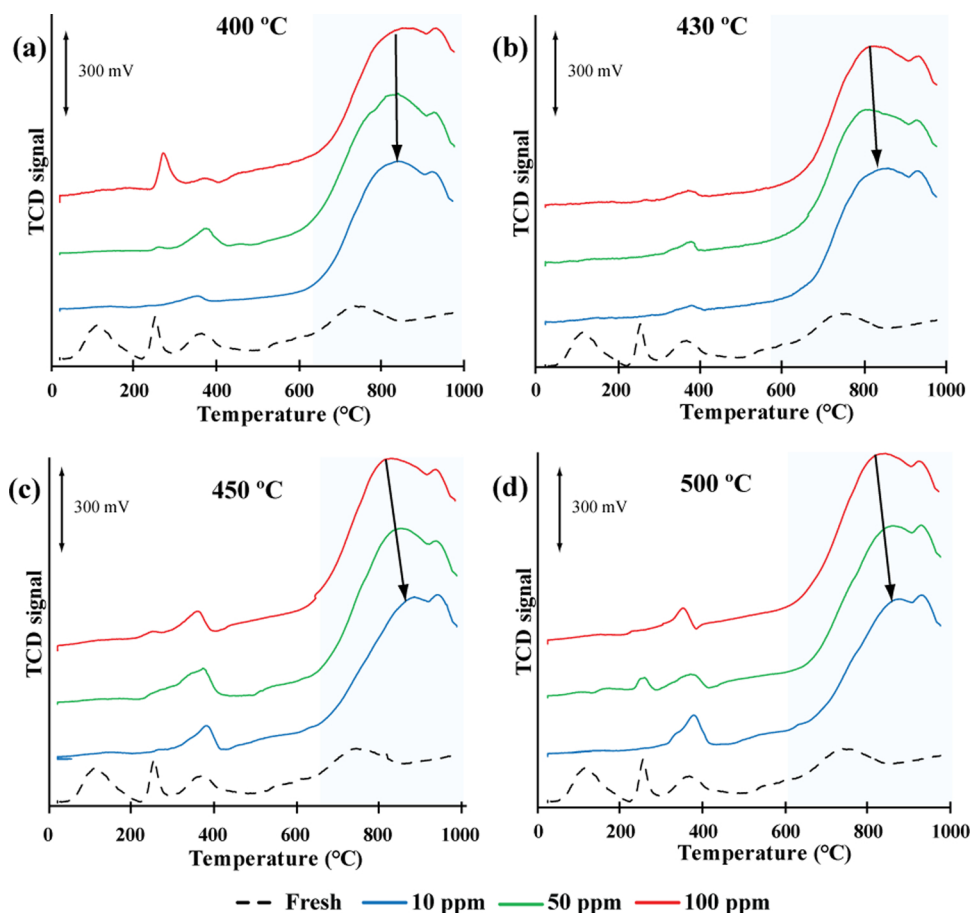


Fig. 5. TPO contour plots of poisoned samples grouped according to temperature. (a) 400 °C, (b) 430 °C, (c) 450 °C and (d) 500 °C. SO₂ concentrations: 10 ppm (blue), 50 ppm (green) and 100 ppm (red). Peaks shown on the shaded background correspond to O₂ and SO₂ desorption (For interpretation of the references to colour in this figure Legend, the reader is referred to the web version of this article).

deactivation in respect of SO₂ concentration. Based on these findings, we could postulate that SO₂ at high concentrations formed less stable sulphates that bound to the catalyst surface and support, while low SO₂ concentrations generated stabler bulk PdSO₄.

4. Conclusions

We studied the rapid ageing process under different simulated ageing conditions to better understand how real-engine results could be reproduced in a laboratory environment. To address this question, we gathered data via multi-gas FTIR analysis, elemental analysis, and TPO tests. Based on our results, we suggest that SO₂ concentration and reaction temperature have a crucial impact on the poisoning mechanism of PdO in MOCs. According to the FTIR measurements, MOC poisoning with lower concentrations of SO₂ resulted in higher CH₄ conversion at the end of the poisoning process. This was in agreement with the elemental analysis results, which suggested the catalysts poisoned with high SO₂ concentrations (50 and 100 ppm) retained a larger quantity of sulphur. Additionally, the TPO data indicated that sulphates formed at higher SO₂ concentrations were less stable than those formed in samples poisoned with a lower SO₂ concentration (10 ppm). This might be related to a spillover phenomenon occurring at higher SO₂ concentrations. At high SO₂ concentrations (50 ppm and 100 ppm), the number of PdO sites available for SO₂ oxidation to SO₃ and ultimately PdSO₄ is limited. In other words, reduced PdO/Pd ratio in the MOC makes spillover to alumina a more feasible route for the oxidation reaction, which leads to more abundant formation of Al₂(SO₄)₃. According to literature, Al₂(SO₄)₃ destabilizes PdSO₄. In contrast, SO₂ in low concentration forms stabler sulphates, which can be attributed to the formation of bulk PdSO₄ and only minor amount of Al₂(SO₄)₃. Furthermore, these samples gather less sulphur and are less subject to

the spillover mechanism. A paucity of spillover leads to higher bypass of SO₂, which results in accumulation of less sulphur in the poisoned catalyst. The results of elemental analysis indicated that some PdO remained in the catalysts after poisoning for 10 h with 10 ppm SO₂. To summarise, SO₂ concentration affects the ratio in which PdSO₄ and Al₂(SO₄)₃ are formed. We also confirmed the previous observations that reaction temperature affects the sulphur poisoning. According to TPO measurements, stabler sulphates are formed at high temperatures (450 and 500 °C) in contrast to temperatures near light-off region (400 and 430 °C).

These findings provide information with regard to how SO₂ concentration and reaction temperature can affect the outcome of rapid ageing in laboratory simulations. Because natural gas contains approximately 1 ppm SO₂, it can be deduced that low concentrations produce similar sulphates. But poisoning times in simulations are prolonged. Thus, to obtain accurate ageing results in the laboratory, the SO₂ concentration should be similar to that of the specific fuel of interest. However, this approach removes the time-savings benefit of simulation. Ultimately, performing a rapid ageing simulation is a compromise between chemical accuracy and poisoning time. The lower the SO₂ concentration, the higher the accuracy. Then again, the fact we were able to achieve satisfactory conversions with 50 ppm SO₂ indicates sufficient conversion could be realized with lower SO₂ concentrations. Overall, our findings can be used to fine-tune laboratory rapid ageing techniques to improve real-engine simulations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

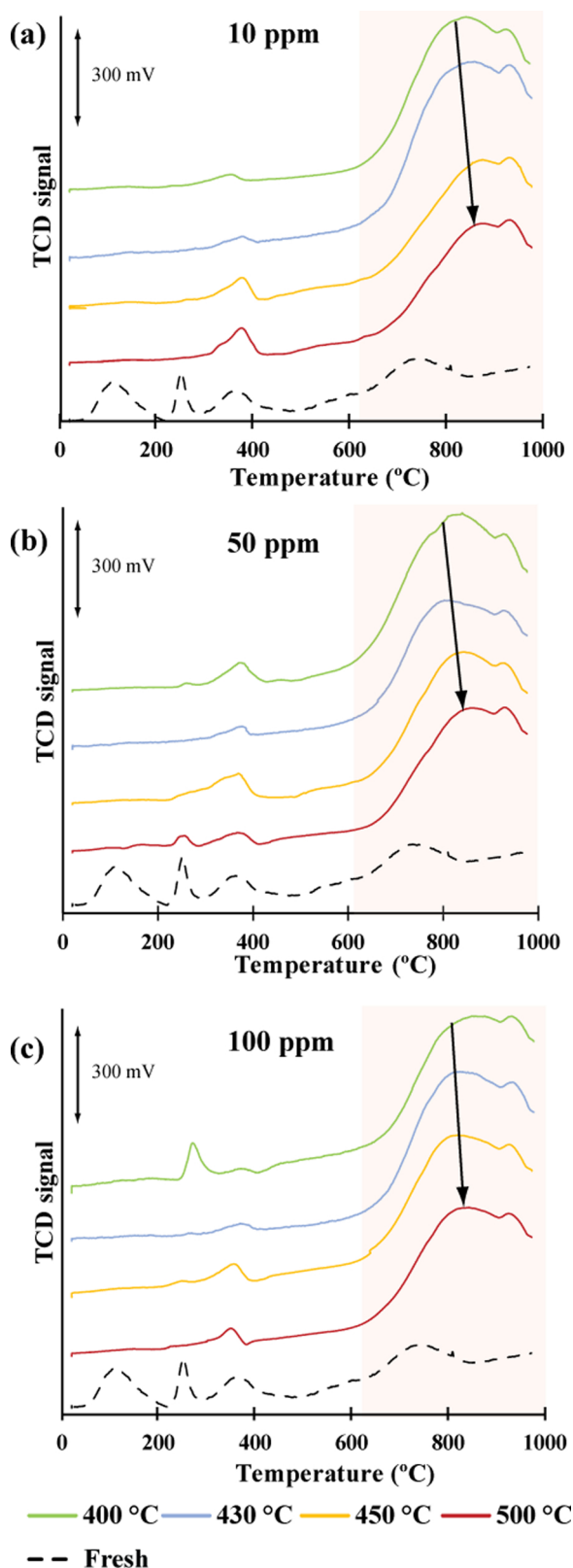


Fig. 6. TPO contour plots of poisoned samples grouped according to SO_2 concentration. (a) 10 ppm, (b) 50 ppm and (c) 100 ppm. Temperatures: 400 °C (light green), 430 °C (light blue), 450 °C (yellow) and 500 °C (red). Peaks shown on the red background correspond to O_2 and SO_2 desorption (For interpretation of the references to colour in this figure Legend, the reader is referred to the web version of this article).

Acknowledgments

The European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement no. 653391 (HDGAS Project) provided funding for the research presented in this paper. We thank laboratory technician Taina Nivajärvi for performing the elemental analysis. The expertise of laboratory technicians Martti Lappalainen and Urpo Rätinen in building and maintaining the flow-reactor device in our research laboratory is greatly appreciated.

References

- [1] The Intergovernmental Panel on Climate Change, Global Warming of 1.5 °C, (2018) https://www.ipcc.ch/publications_and_data/publications_and_data.shtml.
- [2] European Commission, Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, A European Strategy for Low-Emission Mobility, (2016) (Accessed 30 October 2017), <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52016SC0244&from=en>.
- [3] H.M. Cho, B.-Q. He, Spark ignition natural gas engines—a review, *Energy Convers. Manage.* 48 (2007) 608–618, <https://doi.org/10.1016/j.enconman.2006.05.023>.
- [4] P. Gélin, M. Primet, Complete oxidation of methane at low temperature over noble metal based catalysts: a review, *Appl. Catal. B* 39 (2002) 1–37, [https://doi.org/10.1016/S0926-3373\(02\)00076-0](https://doi.org/10.1016/S0926-3373(02)00076-0).
- [5] H.M. Cho, B.-Q. He, Combustion and emission characteristics of a lean burn natural gas engine, *Int. J. Automot. Technol.* 9 (2008) 415–422, <https://doi.org/10.1007/s12239-008-0050-5>.
- [6] S. Faramawy, T. Zaki, A.A.E. Sakr, Natural gas origin, composition, and processing: a review, *J. Nat. Gas Sci. Eng.* 34 (2016) 34–54, <https://doi.org/10.1016/j.jngse.2016.06.030>.
- [7] Working Group I Contribution to the Fifth Assessment Report of the International Panel on Climate Change, *Climate Change 2013: The Physical Science Basis*, Cambridge University Press, New York, 2013.
- [8] European Parliament and the Council of the European Union, Regulation (EC) No 595/2009.
- [9] A.K. Neyestanaki, F. Klingstedt, T. Salmi, D.Y. Murzin, Deactivation of post-combustion catalysts, a review, *Fuel* 83 (2004) 395–408, <https://doi.org/10.1016/j.fuel.2003.09.002>.
- [10] D.L. Mowery, R.L. McCormick, Deactivation of alumina supported and unsupported PdO methane oxidation catalyst: the effect of water on sulfate poisoning, *Appl. Catal. B* 34 (2001) 287–297, [https://doi.org/10.1016/S0926-3373\(01\)00222-3](https://doi.org/10.1016/S0926-3373(01)00222-3).
- [11] D. Ciuparu, M.R. Lyubovsky, E. Altman, L.D. Pfefferle, A. Datye, Catalytic combustion of methane over palladium-based catalysts, *Catal. Rev. Sci. Eng.* 44 (2002) 593–649, <https://doi.org/10.1081/CR-120015482>.
- [12] A.T. Gremminger, H.W. Pereira de Carvalho, R. Popescu, J.D. Grunwaldt, O. Deutschmann, Influence of gas composition on activity and durability of bimetallic Pd-Pt/ Al_2O_3 catalysts for total oxidation of methane, *Catal. Today* 258 (2015) 470–480, <https://doi.org/10.1016/j.cattod.2015.01.034>.
- [13] N. Sadokhina, G. Smedler, U. Nylén, M. Olofsson, L. Olsson, The influence of gas composition on Pd-based catalyst activity in methane oxidation – inhibition and promotion by NO, *Appl. Catal. B* 200 (2017) 351–360, <https://doi.org/10.1016/j.apcatb.2016.07.012>.
- [14] W. Qi, J. Ran, Z. Zhang, J. Niu, P. Zhang, L. Fu, B. Hu, Q. Li, Methane combustion reactivity during the metal→metallic oxide transformation of Pd-Pt catalysts: effect of oxygen pressure, *Appl. Surf. Sci.* 435 (2018) 776–785, <https://doi.org/10.1016/j.apsusc.2017.11.178>.
- [15] P. Hurtado, S. Ordóñez, H. Sastre, F.V. Díez, Combustion of methane over palladium catalyst in the presence of inorganic compounds: inhibition and deactivation phenomena, *Appl. Catal. B* 47 (2004) 85–93, [https://doi.org/10.1016/S0926-3373\(03\)00328-X](https://doi.org/10.1016/S0926-3373(03)00328-X).
- [16] G. Lapisardi, P. Gélin, A. Kaddouri, E. Garbowski, S. Da Costa, Pt-Pd bimetallic catalysts for methane emissions abatement, *Top. Catal.* 42 (2007) 461–464, <https://doi.org/10.1007/s1244-007-0225-8>.
- [17] N.M. Kinnunen, J.T. Hirvi, M. Suvanto, T.A. Pakkanen, Role of the interface between Pd and PdO in methane dissociation, *J. Phys. Chem. C* 115 (2011) 19197–19202, <https://doi.org/10.1021/jp204360c>.
- [18] M.S. Wilburn, W.S. Epling, Sulfur deactivation and regeneration of mono- and bimetallic Pd-Pt methane oxidation catalysts, *Appl. Catal. B* 206 (2017) 589–598, <https://doi.org/10.1016/j.apcatb.2017.01.050>.
- [19] P. Gélin, L. Urfels, M. Primet, E. Tena, Complete oxidation of methane at low temperature over Pt and Pd catalysts for the abatement of lean-burn natural gas fuelled vehicles emissions: influence of water and sulphur containing compounds, *Catal. Today* 83 (2003) 45–57, [https://doi.org/10.1016/S0920-5861\(03\)00215-3](https://doi.org/10.1016/S0920-5861(03)00215-3).
- [20] H. Sharma, V. Sharma, T.D. Huan, Exploring PtSO_4 and PdSO_4 phases: an evolutionary algorithm based investigation, *Phys. Chem. Chem. Phys.* 17 (2015) 18146–18151, <https://doi.org/10.1039/c5cp02658j>.
- [21] S. Ordóñez, J.R. Paredes, F.V. Díez, Sulphur poisoning of transition metal oxides used as catalysts for methane combustion, *Appl. Catal. A* 341 (2008) 174–180, <https://doi.org/10.1016/j.apcata.2008.02.042>.
- [22] N.M. Kinnunen, J.T. Hirvi, K. Kallinen, T. Maunula, M. Keenan, M. Suvanto, Case study of a modern lean-burn methane combustion catalyst for automotive applications: what are the deactivation and regeneration mechanisms? *Appl. Catal. B*

- 207 (2017) 114–119, <https://doi.org/10.1016/j.apcatb.2017.02.018>.
- [23] B. Darif, S. Ojala, M. Kärkkäinen, S. Pronier, T. Maunula, R. Brahm, R.L. Keiski, Study on sulfur deactivation of catalysts for DMDS oxidation, *Appl. Catal. B* 206 (2017) 653–665, <https://doi.org/10.1016/j.apcatb.2017.01.053>.
- [24] D.L. Mowery, M.S. Graboski, T.R. Ohno, R.L. McCormick, Deactivation of PdO–Al₂O₃ oxidation catalyst in lean-burn natural gas engine exhaust: aged catalyst characterization and studies of poisoning by H₂O and SO₂, *Appl. Catal. B* 21 (1999) 157–169, [https://doi.org/10.1016/S0926-3373\(99\)00017-X](https://doi.org/10.1016/S0926-3373(99)00017-X).
- [25] J.K. Lampert, M.S. Kazi, R.J. Farrauto, Palladium catalyst performance for methane emissions abatement from lean burn natural gas vehicles, *Appl. Catal. B* 14 (1997) 211–223, [https://doi.org/10.1016/S0926-3373\(97\)00024-6](https://doi.org/10.1016/S0926-3373(97)00024-6).
- [26] A. Gremminger, P. Lott, M. Merts, M. Casapu, J.-D. Grunwaldt, O. Deutschmann, Sulfur poisoning and regeneration of bimetallic Pd–Pt methane oxidation catalysts, *Appl. Catal. B Environ.* 218 (2017) 833–843, <https://doi.org/10.1016/j.apcatb.2017.06.048>.
- [27] M. Honkanen, J. Wang, M. Kärkkäinen, M. Huuhtanen, H. Jiang, K. Kallinen, R.L. Keiski, J. Akola, M. Vippola, Regeneration of sulfur-poisoned Pd-based catalyst for natural gas oxidation, *J. Catal.* 358 (2018) 253–265, <https://doi.org/10.1016/j.jcat.2017.12.021>.
- [28] N. Sadokhina, G. Smedler, U. Nylén, M. Olofsson, L. Olsson, Deceleration of SO₂ poisoning on PtPd/Al₂O₃ catalyst during complete methane oxidation, *Appl. Catal. B Environ.* 236 (2018) 384–395, <https://doi.org/10.1016/j.apcatb.2018.05.018>.
- [29] M. Keenan, R. Pickett, E. Troncon, I. Nova, M. Suvanto, N. Kinnunen, T. Maunula, K. Kallinen, R. Baert, The catalytic challenges of implementing a Euro VI heavy duty emissions control system for a dedicated lean operating natural gas engine, *Top. Catal.* 62 (2018) 273–281, <https://doi.org/10.1007/s11244-018-1127-7>.
- [30] T. Hamzehlouyan, C.S. Sampara, J. Li, A. Kumar, W.S. Epling, Experimental and kinetic study of SO₂ oxidation on a Pt/γ-Al₂O₃ catalyst, *Appl. Catal. B Environ.* 152–153 (2014) 108–116, <https://doi.org/10.1016/J.APCATB.2014.01.005>.
- [31] T. Hamzehlouyan, C.S. Sampara, J. Li, A. Kumar, W.S. Epling, Kinetic study of adsorption and desorption of SO₂ over γ-Al₂O₃ and Pt/γ-Al₂O₃, *Appl. Catal. B Environ.* 181 (2016) 587–598, <https://doi.org/10.1016/j.apcatb.2015.08.003>.
- [32] J. Li, A. Kumar, X. Chen, N. Currier, A. Yezerets, Impact of Different Forms of Sulfur Poisoning on Diesel Oxidation Catalyst Performance, (2013), <https://doi.org/10.4271/2013-01-0514>.
- [33] M.S. Wilburn, W.S. Epling, SO₂ adsorption and desorption characteristics of bimetallic Pd–Pt catalysts: Pd:Pt ratio dependency, *Catal. Today* 320 (2019) 11–19, <https://doi.org/10.1016/j.cattod.2017.08.054>.
- [34] N.M. Kinnunen, K. Kallinen, T. Maunula, M. Keenan, M. Suvanto, N.M. Kinnunen, K. Kallinen, T. Maunula, M. Keenan, M. Suvanto, Fundamentals of sulfate species in methane combustion catalyst operation and regeneration—a simulated exhaust gas study, *Catalysts* 9 (2019) 417, <https://doi.org/10.3390/catal9050417>.
- [35] D. Ciuparu, F. Bozon-Verduraz, L. Pfefferle, Oxygen exchange between palladium and oxide supports in combustion catalysts, *J. Phys. Chem. B* 106 (2002) 3434–3442, <https://doi.org/10.1021/jp013577r>.
- [36] W.R. Schwartz, L.D. Pfefferle, Combustion of methane over palladium-based catalysts: support interactions, *J. Phys. Chem. C* 116 (2012) 8578, <https://doi.org/10.1021/jp2119668>.
- [37] R.J. Farrauto, J.K. Lampert, M.C. Hobson, E.M. Waterman, Thermal decomposition and reformation of PdO catalysts; support effects, *Appl. Catal. B Environ.* 6 (1995) 263–270, [https://doi.org/10.1016/0926-3373\(95\)00015-1](https://doi.org/10.1016/0926-3373(95)00015-1).
- [38] V.H. Nissinen, N.M. Kinnunen, M. Suvanto, Regeneration of a sulfur-poisoned methane combustion catalyst: structural evidence of Pd₂S formation, *Appl. Catal. B Environ.* 237 (2018) 110–115, <https://doi.org/10.1016/j.apcatb.2018.05.057>.
- [39] N.M. Kinnunen, V.H. Nissinen, J.T. Hirvi, K. Kallinen, T. Maunula, M. Keenan, M. Suvanto, N.M. Kinnunen, V.H. Nissinen, J.T. Hirvi, K. Kallinen, T. Maunula, M. Keenan, M. Suvanto, Decomposition of Al₂O₃-Supported PdSO₄ and Al₂(SO₄)₃ in the regeneration of methane combustion catalyst: a model catalyst study, *Catalysts* 9 (2019) 427, <https://doi.org/10.3390/catal9050427>.